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| <b>(51) International Patent Classification <sup>7</sup> :</b><br><b>C08F 265/06, 20/12, C08K 3/36, 3/22</b>   |  | <b>A1</b> | <b>(11) International Publication Number:</b><br><b>WO 00/05284</b>  |
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| <b>(21) International Application Number:</b> PCT/GB99/02206<br><b>(22) International Filing Date:</b> 9 July 1999 (09.07.99)<br><b>(30) Priority Data:</b><br>9815730.8                      21 July 1998 (21.07.98)                      GB<br><b>(71) Applicant (for all designated States except US):</b> IMPERIAL<br>CHEMICAL INDUSTRIES PLC [GB/GB]; Imperial Chem-<br>ical House, Millbank, London SW1P 3JF (GB).<br><b>(72) Inventors; and</b><br><b>(75) Inventors/Applicants (for US only):</b> ROBERTSON, Graeme<br>[GB/GB]; 29 Pendle Crescent, Billingham, Cleveland TS23<br>2RA (GB). FRASER, Ian, Muir [GB/GB]; 17 St. Nicholas<br>Gardens, Yarm, Cleveland TS15 9SJ (GB).<br><b>(74) Agents:</b> GIBSON, Sara, Hillary, Margaret et al.; ICI Group<br>Intellectual Property, P.O. Box 90, Wilton, Middlesbrough,<br>Cleveland TS90 8JE (GB). |  |           | <b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR,<br>BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD,<br>GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP,<br>KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK,<br>MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI,<br>SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA,<br>ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ,<br>UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD,<br>RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK,<br>ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI<br>patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR,<br>NE, SN, TD, TG).<br><br><b>Published</b><br><i>With international search report.</i> |
| <b>(54) Title:</b> ACRYLIC POLYMER COMPOSITION   |  |           |  |
| <b>(57) Abstract</b><br><br>An abrasion resistant acrylic composition comprises at least 70 % w/w of the residues of at least one polymerisable acrylic monomer, 0.2-5 % w/w of a finely divided compound comprising at least one oxide selected from silicon, titanium, zirconium and aluminium oxides, and 0.2-25 % w/w of at least one linking compound which is miscible with said polymerisable acrylic monomer and which is capable of bonding to the surface of the oxide compound. The acrylic composition may be thermoformed whilst retaining its abrasion resistant surface properties.   |  |           |  |

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### Acrylic Polymer Composition

The present invention relates to an abrasion resistant polymer composition and a process for its preparation.

Acrylic sheet materials are widely used for building and glazing applications and to form various shaped articles such as baths, sinks, vanity units and shower trays. The abrasion resistance of the acrylic sheet used in such applications is normally required to be as high as possible. One method that is currently used to improve the abrasion resistance of acrylic surfaces involves the application of an abrasion resistant coating to the surface of an acrylic sheet. The coating is typically applied in solution to the acrylic sheet and is then cured, for example by radiation (UV), solvent evaporation or by thermal curing. For example, EP-A-571808 discloses antifogging film, plates and articles comprising an acrylic polymer support and a polymerised and UV reticulated abrasion resistant coating containing acrylic monomers and hydrophilic metal oxide(s). Examples of components within the coating that are thought to provide the abrasion resistant property are titanium, silica, aluminium compounds. Although abrasion-resistant coatings can enhance the performance of acrylic surfaces against abrasion, their use on acrylic sheet which is to be shaped, e.g. by thermoforming, may be limited by the relatively inelastic nature of the coating, which may cause cracking of the coating as the surface is deformed.

Conventional coating technology requires a two step process: polymerising the sheet followed by coating and curing the abrasion resistant formulation. In practice, this often requires a clean room environment to ensure no dust particles become incorporated into the surface layer. There is therefore a significant manufacturing advantage to be gained for an abrasion resistant product which may be delivered in a one-step process.

Curable acrylic compositions containing a high proportion of a mineral filler, such as silica or alumina particles, are well known. These compositions are typically used to form articles such as kitchen sinks or worktops by mixing with a suitable thermal initiator and then pumping them into a heated mould whereupon they are cured to form a solid and inflexible opaque moulded article. These articles generally have a relatively high resistance to abrasion compared to unfilled acrylic sheets of the type which are suitable for thermoforming. The addition of similar fillers at much lower levels to acrylic sheet materials may give some abrasion resistance properties but the polymer formed is hazy

and hence has poor optical properties.

It is therefore an object of the invention to provide an acrylic article which has better resistance to abrasion than unfilled acrylic materials but which has acceptable optical properties for some typical sheet applications.

- 5 Accordingly, in a first aspect, the present invention provides an acrylic composition comprising at least 70% w/w of the residues of at least one polymerisable acrylic monomer, 0.2 - 5% w/w of a finely divided compound comprising at least one oxide selected from silicon, titanium, zirconium and aluminium oxides, and 0.2 - 25% w/w of at least one linking compound which is miscible with said polymerisable acrylic monomer  
10 and which is capable of bonding to the surface of the oxide compound.

- In a second aspect the present invention provides a polymerisable composition comprising at least 70% w/w of at least one polymerisable acrylic monomer, 0.2 - 5% w/w of a finely divided compound comprising at least one oxide selected from silicon, titanium, zirconium and aluminium oxides, and 0.2 - 25% w/w of at least one linking compound  
15 which is miscible with said polymerisable acrylic compound and which is capable of bonding to the surface of the oxide compound.

In a third aspect the present invention provides a process for forming an acrylic composition comprising the steps of:

- (a) mixing together:
- 20 (i) 70 - 99.5 % w/w of a polymerisable acrylic monomer or a solution of a polymer in a polymerisable acrylic monomer with
- (ii) 0.5 - 30% w/w of a dispersion comprising 20 - 50% w/w of a finely divided compound selected from the oxides of silicon, titanium, zirconium or aluminium and 50 - 80% of a linking compound least one linking compound  
25 which is miscible with said polymerisable acrylic compound and which is capable of bonding to the surface of the oxide compound;
- (b) adding to said mixture a quantity of one or more initiator(s) which is sufficient to initiate polymerisation of the acrylic monomer under the conditions used; and
- (c) causing the acrylic monomer to polymerise.

Although dispersions of colloidal silica particles for example, in e.g. hydroxyethyl methacrylate are known for use in coating compositions used to provide abrasion resistant coatings on acrylic surfaces, it has been surprisingly found that the addition of such a composition containing an abrasion resistant component to the monomer(s) used to make the acrylic polymer before polymerisation results in a polymer with good optical properties and also improved abrasion resistant properties compared to the unmodified polymer.

The polymerisable acrylic monomers are alkyl (alk)acrylic acids and esters thereof, including functionalised monomers such as hydroxy, halogen or amine functionalised acrylate or methacrylate monomers. Preferably the monomer(s) comprise one or more alkyl acrylates, alkyl methacrylates or acrylic or methacrylic acid, e.g. methyl, ethyl, hydroxyethyl, butyl, 2-ethylhexyl, cyclohexyl or phenyl esters of acrylic acid or methacrylic acid. One preferred acrylic material comprises a homopolymer or copolymer of methyl methacrylate comprising 80 - 100% of methyl methacrylate residues and 0 - 20% of an alkyl acrylate or methacrylate selected from those materials listed above.

The at least one linking compound is miscible with the acrylic monomer(s) and preferably contains at least one functional group such as an acrylate or methacrylate group which may be copolymerisable with the acrylic monomers. When more than one functional acrylate or methacrylate group is present, the linking compound may be capable of providing a cross-linking site in the acrylic polymer. The linking compound is also capable of bonding to the surface of the oxide compound and this is conveniently achieved by the use of compounds containing polar groups, e.g. having hydroxyl functionality. Preferred compounds are hydroxyl or other polar group-containing acrylate or methacrylate compounds although other compounds may also be suitable. Suitable compounds include hydroxyethyl methacrylate (HEMA), hexanediol diacrylate, tripropylglycol methacrylate, ethylene glycol monopropylether, 3-aminopropyl trimethoxysilane and ethanolamine or mixtures thereof. Some compounds may perform the function of the linking compound adequately whilst having certain disadvantages in certain applications, e.g. the use of coloured compounds or compounds which develop a colour under the conditions of manufacture of the composition or any article made therefrom may be unsuitable when a clear product is required.

The finely divided oxide compound preferably has an average particle size between 1 and 50 nm, more preferably between 5 and 35 nm. It is present at 0.2 - 5% in the composition, more preferably at 0.5 to 3% by weight. A preferred oxide compound is colloidal silica. The oxide compound is preferably added to the acrylic monomer or polymer/monomer solution in the form of a dispersion in the linking compound. Suitable  
5 dispersions are available commercially for use as coating compositions to provide abrasion resistant coatings. Examples of suitable commercial dispersions include the HIGHLINK™ compounds available from Clariant, e.g. Highlink OG 100-30. The ratio of said linking compound to said finely divided oxide is preferably in the range 1:1 - 5:1  
10 (more preferably 2:1 - 4:1) by weight. The dispersion is preferably present at 0.2 to 10%, more preferably 2 to 8% by weight in the polymerisable composition.

The acrylic compositions can be made by conventional free radical, anionic or other polymerisation techniques, for example bulk, solution or suspension with the addition of suitable initiators and optionally chain transfer agents and/or other additives such as  
15 cross-linking additives, fillers, pigments, plasticisers, impact modifiers, stabilisers etc. Therefore the monomer(s) are caused to polymerise by initiating the polymerisation reaction, normally by means of activating the added initiator, and maintaining suitable conditions, e.g. an elevated temperature, pressure etc until the required degree of polymerisation has been achieved. Such methods are already very well known to the  
20 skilled person and a large number of such methods exist in the art. As one preferred option, free-radical polymerisation is used, e.g. in a bulk polymerisation process used in the well-known cell-casting method of manufacturing high molecular weight acrylic sheets in which a (mixture of) polymerisable monomer(s), optionally with polymer dissolved therein to form a syrup, is mixed with an initiator or mixture of initiators and other additives  
25 and filled either into the gap between two glass plates which are separated by a gasket or into a bag or other mould. The polymerisation reaction is then thermally initiated and the polymer allowed to form and cure at elevated temperature. The acrylic composition of the present invention may be in the form of sheets, which may be suitable for shaping by e.g. (thermo)forming, or of powders or pellets, which may be extruded. When a powdered or  
30 pelleted compound is required then the method of polymerising the polymer may also be selected from suspension polymerisation, solution polymerisation or by crushing or

pelletising a bulk polymerised product. Methods of forming acrylic polymers by suspension or solution polymerisation are well known in the art and therefore need not be further described.

The present invention is illustrated by reference to the following examples.

5 Example 1 Preparation of cast polymethylmethacrylate (PMMA) sheet

A mixture comprising 2,2 - azobisisobutyronitrile (AIBN) (0.08% by weight), HIGHLINK™ OG 100-30 (from Clariant) which is a dispersion of 30% by weight colloidal silica of a particle size 13-30 nm in HEMA (2.5% by weight), with the balance of the composition being made up of a standard PMMA syrup comprising a solution of PMMA in  
10 methylmethacrylate (MMA) monomer was mixed using a high shear mixer at maximum setting for 1 minute. The mixture was placed in a cell comprising two glass sheets spaced 3.2 mm apart from each other by a non metallic gasket. The cell was sealed and immersed in a water bath at 45 °C for 20 hours. The mixture was then post cured for 2 hours at 60 °C followed by 2 hours at 80 °C, followed by heating at a rate of 0.5 °C /min up  
15 to 118 °C and held at 118 °C for 1 hour. The cell was then cooled and the glass sheets removed to release the resulting cast PMMA sheet.

50 mm square samples of the cast PMMA were abraded by applying to their surface a rotating 33 mm diameter circular abrasive disc comprising aluminium oxide bonded in resin fibres ("ROLOC FINE GREEN" from 3M company) for 60 seconds at a constant 180  
20 rpm under loading forces of 1, 10 and 20 Newtons (N) respectively. The abrasion resistance of each sample was estimated by determining the light transmission and haze before and after the abrasion treatment using a spectrophotometer in accordance with ASTM D1925-76. The results are shown in the table.

Example 2

25 A cast PMMA sheet was made as described in example 1 using only 0.5% w of the Highlink in the formulation. Testing was carried out as before at a loading of 20N.

Example 3 (Comparative) Preparation of coated PMMA samples

A 3 mm thick sample of cast PMMA sheet was coated with a mixture of HIGHLINK OG

100-30 and 0.2% w/w/ of AIBN initiator at various wet thicknesses of 100, 50, 24 and 12 microns and cured. The resulting coatings were poorly adhered to the substrate and showed evidence of cracking and for this reason they were not tested. In order to improve the coating properties, a coating was formulated from a trifunctional aliphatic polyester urethane acrylate oligomer (Craynor™ 929 from Cray Valley) diluted to 50% w/w in hexanediol diacrylate with the HIGHLINK composition at a ratio of 1:1 by weight. A photoinitiator (Darocur™ 1173) was added at 2% w/w prior to coating. The coating was applied at a wet thickness of 4 microns and cured under UV light in a commercial UV coating apparatus. The coated samples were then tested as described in example 1.

10 The results show that the abrasion resistance performance was comparable to that of Examples 1 & 2.

#### Example 4 (comparative)

50 mm square samples of standard cast PMMA coated at 4 microns wet thickness with UVECRYL™ 29203 (UCB Resins), a UV curable aliphatic urethane acrylate abrasion resistant coating, were prepared and abraded on the coated surface. The optical properties were measured as described in Example 1. The results show that the PMMA of the present invention is at least comparable in abrasion resistance performance to PMMA coated with "UVECRYL 29203".

#### Example 5 (comparative)

20 50 mm square samples of unmodified cast PMMA, i.e. PMMA syrup polymerised without the presence of the oxide compound, were abraded and the optical properties measured as described in Example 1. The results show that the abrasion resistance of the samples of the invention are superior to that of the unmodified PMMA, in that the light transmission remains greater and the haze less than that of the unmodified PMMA at all loading levels.

#### Example 6 (comparative)

A PMMA sample was cast from a similar PMMA in MMA syrup which had been mixed with cristobalite silica (mean particle size 6 nm) dispersed as a slurry in MMA, i.e. so that the linking compound of the invention was not present. The amount of slurry used gave a total concentration of 0.75 %w/w of silica in the total acrylic mixture. The mixture was initiated and polymerised as before. The resulting sample of acrylic polymer was abraded



and tested as described in Example 1. The results show that this material had a much higher haze value than the others and that the light transmission and haze degraded with abrasion.

| Loading (N) | Light Transmission |      |      |      | Haze |      |      |      |
|-------------|--------------------|------|------|------|------|------|------|------|
|             | 0                  | 1    | 10   | 20   | 0    | 1    | 10   | 20   |
| Ex 1        | 90.4               | 88.8 | 87.3 | 85.9 | 1.6  | 9.7  | 13.5 | 16.6 |
| Ex 2        | 92.3               |      |      | 83.5 | 0.7  |      |      | 24.5 |
| Ex 3 (comp) | 92.1               | 90.0 | 89.1 | 84.2 | 0.4  | 6.0  | 13.0 | 22.7 |
| Ex 4 (comp) | 92.1               | 88.9 | 85.9 | 84.5 | 0.1  | 8.5  | 10.0 | 27.0 |
| Ex 5 (comp) | 92.4               | 86.7 | 80.9 | 82.5 | 0.2  | 19.9 | 34.9 | 31.6 |
| Ex 6 (comp) | 87.0               |      | 85.3 | 81.1 | 15.7 |      | 21.9 | 36.9 |

#### Example 7 Thermoforming of samples

- 5 PMMA sheet of Examples 1, 3 and 5, was (thermo)formed by placing a mould and sheet assembly in an electric oven preheated at 180 °C for 30 minutes. A two-stage rotary vacuum pump was attached to the mould and maximum vacuum applied. When thermoforming had been completed the assembly was cooled under vacuum until the PMMA surface temperature had dropped to 80 °C or below. The moulded article was
- 10 then removed from the mould. The resulting mouldings from Examples 1 and 5 were satisfactory in appearance whilst that of Example 3 was shown not to have been fully drawn and cracks were visible on the drawn surface.

Claims

- 1 An acrylic composition comprising at least 70% w/w of the residues of at least one polymerisable acrylic monomer, 0.2 - 5% w/w of a finely divided compound comprising at least one oxide selected from silicon, titanium, zirconium and aluminium oxides, and 0.2 - 25% w/w of at least one linking compound which is miscible with said polymerisable acrylic compound and which is capable of bonding to the surface of the oxide compound.
- 2 An acrylic composition as claimed in claim 1, wherein the linking compound contains at least one functional group which is copolymerisable with the acrylic monomers and a polar group which is capable of bonding to the surface of the oxide compound.
- 3 An acrylic composition as claimed in claim 2, wherein the linking compound comprises a monofunctional or polyfunctional acrylate or methacrylate compound which additionally contains a polar hydroxyl group.
- 4 An acrylic composition as claimed in claim 3, wherein the linking compound is selected from hydroxyethylmethacrylate, hexanedioldiacrylate or tripropylglycolmethacrylate.
- 5 An acrylic composition as claimed in any one of claims 1 - 4, wherein the finely divided oxide compound comprises colloidal silica.
- 6 An acrylic composition as claimed in any preceding claim, wherein the finely divided oxide compound has an average particle size between 1 and 50 nm.
- 7 An acrylic composition as claimed in any preceding claim, wherein the ratio of said linking compound to said finely divided oxide is preferably in the range 1:1 - 5:1 by weight.
- 8 A polymerisable composition comprising at least 70% w/w of at least one polymerisable acrylic monomer, 0.2 - 5% w/w of a finely divided compound comprising at least one oxide selected from silicon, titanium, zirconium and aluminium oxides, and 0.2 - 25% w/w of at least one linking compound which is miscible with said polymerisable acrylic compound and which is capable of bonding to the surface of the oxide compound.
- 9 a process for forming an acrylic composition comprising the steps of:
  - (a) mixing together

- (i) 70 - 99.5 % w/w of a polymerisable acrylic monomer or a solution of a polymer in a polymerisable acrylic monomer with
  - (ii) 0.5 - 30% w/w of a dispersion comprising 20 - 50% w/w of a finely divided compound selected from the oxides of silicon, titanium, zirconium or aluminium
  - (b) adding to said mixture a quantity of one or more initiator(s) which is sufficient to initiate polymerisation of the acrylic monomer under the conditions used; and
  - (c) causing the acrylic monomer to polymerise.
- 10 An acrylic composition as claimed in any of claims 1 - 8 which is in the form of a sheet, powder, pellet or bead.

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

|   |   |  |
|---|---|--|
| Applicant's or agent's file reference<br><b>MTW50638/WO</b> | <b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below. |  |
| International application No.<br><b>PCT/GB 99/ 02206</b>    | International filing date (day/month/year)<br><b>09/07/1999</b>   | (Earliest) Priority Date (day/month/year)<br><b>21/07/1998</b> |
| Applicant<br><b>IMPERIAL CHEMICAL INDUSTRIES PLC et al.</b> |   |  |

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

## 1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

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2. ☐

**Certain claims were found unsearchable** (See Box I).

3. ☐

**Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

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6. The figure of the **drawings** to be published with the abstract is Figure No.

as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.



None of the figures.

# INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/GB 99/02206

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F265/06 C08F20/12 C08K3/36 C08K3/22

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F C09D C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
|------------|--|-----------------------|
| X          | EP 0 571 808 A (ATOCHEM ELF ITALIA)<br>1 December 1993 (1993-12-01)<br>cited in the application<br>examples 3,4<br>claims      | 1-14                  |
| X          | EP 0 659 530 A (ROEHM GMBH)<br>28 June 1995 (1995-06-28)<br>examples   | 1-14                  |
| X          | WO 96 26238 A (ARISTECH CHEMICAL CORP)<br>29 August 1996 (1996-08-29)<br>page 28, line 11 - line 16<br>examples 3,5<br>claim 1 | 1-14                  |
|            | ---  |                       |
|            | -/--   |                       |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

14 October 1999

Date of mailing of the international search report

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Name and mailing address of the ISA

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 99/02206

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages                    | Relevant to claim No. |
|------------|---|-----------------------|
| X          | WO 97 14749 A (ICI ACRYLICS INC)<br>24 April 1997 (1997-04-24)<br>example 1<br>claim 1                | 1-3, 14               |
| X          | EP 0 685 511 A (ATOHAAS HOLDING CV)<br>6 December 1995 (1995-12-06)<br>abstract<br>examples<br>claims | 1-3, 14               |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB ' /02206

| Patent document<br>cited in search report |   | Publication<br>date | Patent family<br>member(s)  | Publication<br>date  |
|---|---|---------------------|---|--|
| EP 0571808                                | A | 01-12-1993          | IT 1255297 B<br>AT 141316 T<br>CA 2096997 A<br>CN 1083833 A<br>DE 69303978 D<br>DE 69303978 T<br>ES 2093312 T<br>FI 932398 A<br>JP 7034005 A<br>NO 931892 A<br>US 5342683 A | 26-10-1995<br>15-08-1996<br>28-11-1993<br>16-03-1994<br>19-09-1996<br>02-01-1997<br>16-12-1996<br>28-11-1993<br>03-02-1995<br>29-11-1993<br>30-08-1994 |
| EP 0659530                                | A | 28-06-1995          | DE 4343868 A<br>CZ 9403271 A<br>HU 69756 A<br>PL 306480 A<br>RU 2097186 C<br>SI 9400451 A<br>SK 156894 A  | 29-06-1995<br>13-12-1995<br>28-09-1995<br>26-06-1995<br>27-11-1997<br>30-06-1995<br>11-07-1995   |
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## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C.20231  
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

|  |  |
|--|--|
| <b>Date of mailing (day/month/year)</b><br>14 March 2000 (14.03.00)          |  |
| <b>International application No.</b><br>PCT/GB99/02206                       | <b>Applicant's or agent's file reference</b><br>MTW50638/WO      |
| <b>International filing date (day/month/year)</b><br>09 July 1999 (09.07.99) | <b>Priority date (day/month/year)</b><br>21 July 1998 (21.07.98) |
| <b>Applicant</b><br>ROBERTSON, Graeme et al                                  |  |

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

12 February 2000 (12.02.00)

☐ in a notice effecting later election filed with the International Bureau on:
2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

|  |   |
|--|---|
| <b>The International Bureau of WIPO</b><br>34, chemin des Colombettes<br>1211 Geneva 20, Switzerland<br>Facsimile No.: (41-22) 740.14.35 | <b>Authorized officer</b><br>S. Mafla<br>Telephone No.: (41-22) 338.83.38 |
|--|---|



## PATENT COOPERATION TREATY

## PCT

REC'D 21 NOV 2000

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

15

(PCT Article 36 and Rule 70)



|  |   |  |
|--|---|--|
| Applicant's or agent's file reference<br>DPW/EM/R418                                       | <b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) |  |
| International application No.<br>PCT/GB99/02206  | International filing date (day/month/year)<br>09/07/1999  | Priority date (day/month/year)<br>21/07/1998 |
| International Patent Classification (IPC) or national classification and IPC<br>C08F265/06 |   |  |
| Applicant<br><b>IMPERIAL CHEMICAL INDUSTRIES PLC et al INEOS Acrylics UK Limited</b>       |   |  |

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 7 sheets, including this cover sheet.  
☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☐ Certain observations on the international application

|   |  |
|---|--|
| Date of submission of the demand<br>12/02/2000  | Date of completion of this report<br>17. 11. 00  |
| Name and mailing address of the international preliminary examining authority:<br> European Patent Office<br>D-80298 Munich<br>Tel. +49 89 2399 - 0 Tx: 523656 epmu d<br>Fax: +49 89 2399 - 4465 | Authorized officer<br>Barker, S<br>Telephone No. +49 89 2399 8526<br> |

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/02206

## I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

**Description, pages:**

1-7 as originally filed

**Claims, No.:**

1-10 as received on 12/09/2000 with letter of 12/09/2000

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
  - ☐ the language of publication of the international application (under Rule 48.3(b)).
  - ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).
3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:
- ☐ contained in the international application in written form.
  - ☐ filed together with the international application in computer readable form.
  - ☐ furnished subsequently to this Authority in written form.
  - ☐ furnished subsequently to this Authority in computer readable form.
  - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
  - ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.
4. The amendments have resulted in the cancellation of:
- ☐ the description, pages:
  - ☐ the claims, Nos.:
  - ☐ the drawings, sheets:
5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/02206

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

### 1. Statement

|                               |      |             |
|-------------------------------|------|-------------|
| Novelty (N)                   | Yes: | Claims      |
|                               | No:  | Claims 1-10 |
| Inventive step (IS)           | Yes: | Claims      |
|                               | No:  | Claims 1-10 |
| Industrial applicability (IA) | Yes: | Claims 1-10 |
|                               | No:  | Claims      |

2. Citations and explanations  
**see separate sheet**

## VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:  
**see separate sheet**

Re. part V

- 1). a) The subject matter of the present claims 1-10 is considered to lack novelty for the following reasons. Claims 1-10 do not fulfill the requirements of Art.33(1) and (2) PCT.
- b) Independent claims 1, and 8 have been amended to include the words, "wherein the composition excludes a level of polymerisable acrylic monomer of 70%w/w." Notwithstanding that doubts are expressed below at point 6 as to whether the amendment is permissible, even if the amendment is accepted, it does not make the subject matter of the subject matter of the claims 1-10 new over the disclosure in EP 0571808 (D1) which is cited in the International Search Report (ISR). D1 discloses polymerised compositions which comprise:
  - (a) 50-70 wt.% of a (meth)acrylate of an alkyl, cycloalkyl, polycycloalkyl or alkylidene as defined. Such monomers correspond to the polymerisable acrylic monomer of claims 1,8 and 9.
  - (b) 10-30 wt.% of (meth)acrylate of C<sub>2</sub>-C<sub>6</sub> hydroxyalkyl which corresponds to the linking compound of present claims 1-4 and 9 - see also the present description at page 3, line 16 et seq. In particular, D1 mentions hydroxyethylmethacrylate (HEMA) as a preferred example of monomer (b) (see page 3, lines 41-43). Accordingly, the linking compound of claims 1-4,8 and 9 are anticipated.
  - (c) 10-30 wt.% of (meth)acrylic acid or its salt. Note is made that such monomer (c) is also a polymerisable acrylic monomer according to present claims 1,8 and 9 as is discussed in the present description at page 3, lines 8-13. Accordingly, the combined levels of components (a) and (c) of D1, where the permitted maximum of (a), i.e. 70 wt.%, is present would inevitably result in a level of combined polymerisable monomer above 70 wt.% therefore anticipating that feature of claims 1 and 8 as amended.
  - (d) 1-10 wt.% of a reticulation (cross-linking) agent. Such compounds while not mentioned in present claims 1,8 and 9 are not excluded by it on account of the "open" (comprising) form of these claims.
  - (e) 0.01 to 3 wt.% of hydrophilic colloidal metal oxides, in particular silica (see D1 at page 2, line 23). This disclosure covers the 0.2-5% w/w of finely divided oxide compound recited in present claims 1,8 and 9 and the embodiments defined at claims 5 and 6.

- (f) optionally up to 0.06 wt.% of U.V. initiator is not excluded by the form of the present claims.
- c) The subject matter of present claim 7 is anticipated by the ratio of the upper limits of the components (b) and (e) of D1. The subject matter of claim 10 is anticipated by the reference to the preparation of plates in D1 at page 4, lines 1-3.
- 2). a) The subject matter of claims 1-10 is further considered to lack novelty over the disclosure in WO 96/26238 A (D3) (see ISR) which discloses (see page 5, line 18 to page 6, line 32) filled polymethylmethacrylate compositions comprising filler, thixotropic agent and crosslinking agent. Accordingly, the requirements of Art.33(1) and (2) PCT are not met.
- b) The filler is alumina trihydrate (ATH) present at levels which can be as low as 20% wt. of the finished product (see page 8, lines 23-25).
- c) The compositions, which are formed from syrups containing prepolymerised polymethylmethacrylate dissolved in methyl methacrylate monomer (MMA), further contain a crosslinking agent exemplified at page 9, line 9 et seq. Of the examples given, several would appear to be compounds which would also act as linking compounds in the sense of being miscible with the acrylic monomer (MMA) and being capable of bonding to the surface of the oxide compound. See for instance hydroxyethyl methacrylate, hydroxypropyl methacrylate and ethylene glycol dimethacrylate mentioned at page 9, lines 21-24. The crosslinking agent is present at levels of up to 0.6 mole percent based on the MMA. Thus, values within the range of 0.2-25 wt.% as recited in the present independent claims appear to be disclosed.
- d) The thixotropic agent present is preferably fumed silica having a particle size of 7-30 nm and present in an amount of 0.1-3.5 % by weight (see page 5, last six lines).
- e) Where the level of filler is 20% wt., the amount of MMA syrup or polymerised MMA syrup would exceed 70 wt.% wt. Moreover, the ATH filler of D3 is not specifically excluded by the wording of the present claims 1,8 and 9 which are cast in open ("comprising") form and make no requirement that three percentages expressed in each claim must total 100%.
- 3). a) The subject matter of claims 1-9 is considered to lack novelty over the disclosure in EP 0685511 A (D5) which is cited in the ISR. Accordingly, those

claims do not meet the requirements of Arts.33(1) and (2) PCT)

b) D5 discloses a composition for coating articles formed from acrylic resins to provide scratch-resistance to the articles. The composition comprises an acrylic monomer in an amount of 40-98.5 % wt. The composition further comprises a monomer b) which is preferably (see claim 7) hydroxy ethyl methacrylate and therefore corresponds to the linking compound of the present claims 1. The monomer b) is present in an amount of 1-20 wt.% thus being within the weight range of the linking compound of the present claims. The compositions may further contain as an optional component up to 3% wt of d), a colloidal silica of particle size less than 20 nm (see column 4, lines 2-7). The compositions further contain 0.5-10 % wt. of UV-light initiator. Where, 3% wt. of colloidal silica is selected and the amount of initiator is towards the lower end of the range disclosed, then the amount of monomer a) present would inevitably be greater than 70% wt. Accordingly, all features of claims 1-9 are disclosed.

c) As D5 also deals with the problem of providing scratch resistance, it may well prove of relevance in future with regard to amended claims. However, as D5 teaches a coating for articles, it is not considered to render the subject matter of present claim 10. (Art.33(1) and (c) PCT)

4). As to the other documents cited in the ISR, the following points arise with regard to the provisions of Art.33(1),(2) and (3) PCT:

a) EP 0659530 A (D2) discloses high filler-content resin moulding compositions which further contain finely divided silica to prevent undesired settling of the filler. However, as the finely divided silica is added at around the same time as the filler, the resulting monomer content of the formed composition is significantly below 60 wt. %. Accordingly, there is no disclosure of either a polymerisable composition according to claim 8, a composition according to claim 1 or process according to claim 9. Moreover, the subject matter of present independent claims 1,8 and 9 is also not rendered obvious by D2.

b) WO 97/14749 (D4) discloses the preparation of a "granite-effect" polymethyl methacrylate resin composition wherein black- and white coloured polymethyl methacrylate resins are prepared and subsequently ground. The ground resins, a part of which is described as fines, are added in a second stage to MMA and other components including ethylene glycol dimethacrylate as crosslinking agent but which is considered to be a linking compound within the meaning of the present

independent claims. However, study of example 1 at page 15 concludes that the 0.51 g of ethylene glycol dimethacrylate used corresponds to an amount of such "linking compound" of only 0.17% wt. which is below the minimum of linking compound required in the present claims; thus novelty is recognised. As D4 contains no discussion of the amounts of cross-linking agent used in the second stage polymerisation, inventive step is also not challenged on the basis of D4.

- 5). The subject matter of the present claims is considered to be capable of industrial application. (Arts.33(1) and (4) PCT)

Re. part VII

- 6). The presence of the words "wherein the composition excludes a level of polymerisable acrylic monomer of 70% w/w" is considered to a non-permissible disclaimer which introduces wording into the application which extends beyond the disclosure in the international application as filed. While the present IPEA does permit the introduction of disclaimers in the case where the prior art which is disclaimed is coincidental, in the present case, the prior art documents D1, D3 and D5 are all considered to be of such relevance to both novelty and inventive step, that disclaimers are not acceptable. (Art.34(2)(b) PCT)

12-09-2000

PCT/GB99/02206

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## CLAIMS

- 1 An acrylic composition comprising at least 70% w/w of the residues of at least one polymerisable acrylic monomer, 0.2 - 5% w/w of a finely divided compound comprising at least one oxide selected from silicon, titanium, zirconium and aluminium oxides, and 0.2 - 25% w/w of at least one linking compound which is miscible with said polymerisable acrylic compound and which is capable of bonding to the surface of the oxide compound, wherein the composition excludes a level of polymerisable acrylic monomer of 70% w/w.
- 2 An acrylic composition as claimed in claim 1, wherein the linking compound contains at least one functional group which is copolymerisable with the acrylic monomers and a polar group which is capable of bonding to the surface of the oxide compound.
- 3 An acrylic composition as claimed in claim 2, wherein the linking compound comprises a monofunctional or polyfunctional acrylate or methacrylate compound which additionally contains a polar hydroxyl group.
- 4 An acrylic composition as claimed in claim 3, wherein the linking compound is selected from hydroxyethylmethacrylate, hexanedioldiacrylate or tripropylglycolmethacrylate.
- 5 An acrylic composition as claimed in any one of claims 1 - 4, wherein the finely divided oxide compound comprises colloidal silica.
- 6 An acrylic composition as claimed in any preceding claim, wherein the finely divided oxide compound has an average particle size between 1 and 50 nm.
- 7 An acrylic composition as claimed in any preceding claim, wherein the ratio of said linking compound to said finely divided oxide is preferably in the range 1:1 - 5:1 by weight.
- 8 A polymerisable composition comprising at least 70% w/w of at least one polymerisable acrylic monomer, 0.2 - 5% w/w of a finely divided compound comprising at least one oxide selected from silicon, titanium, zirconium and aluminium oxides, and 0.2 - 25% w/w of at least one linking compound which is miscible with said polymerisable acrylic compound and which is capable of bonding to the surface of the oxide compound, wherein the composition excludes a level of polymerisable acrylic monomer of 70% w/w.
- 9 a process for forming an acrylic composition comprising the steps of:
  - (a) mixing together
    - (i) 70 - 99.5 % w/w of a polymerisable acrylic monomer or a solution of a polymer in a polymerisable acrylic monomer with
    - (ii) 0.5 - 30% w/w of a dispersion comprising 20 - 50% w/w of a finely divided



12-09-2000

PCT/GB99/02206

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compound selected from the oxides of silicon, titanium, zirconium or aluminium

(b) adding to said mixture a quantity of one or more initiator(s) which is sufficient to initiate polymerisation of the acrylic monomer under the conditions used; and  
(c) causing the acrylic monomer to polymerise.

- 10 An acrylic composition as claimed in any of claims 1 - 8 which is in the form of a sheet, powder, pellet or bead.

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JC02 Rec'd PCT/PTO 22 JAN 2001

AMENDED CLAIMS FROM  
INTERNATIONAL PRELIMINARY EXAMINATION REPORT

Claims

- 1 An acrylic composition comprising at least 70% w/w of the residues of at least one polymerisable acrylic monomer, 0.2 - 5% w/w of a finely divided compound comprising at least one oxide selected from silicon, titanium, zirconium and aluminium oxides, and 0.2 - 25% w/w of at least one linking compound which is miscible with said polymerisable acrylic compound and which is capable of bonding to the surface of the oxide compound.
- 2 An acrylic composition as claimed in claim 1, wherein the linking compound contains at least one functional group which is copolymerisable with the acrylic monomers and a polar group which is capable of bonding to the surface of the oxide compound.
- 3 An acrylic composition as claimed in claim 2, wherein the linking compound comprises a monofunctional or polyfunctional acrylate or methacrylate compound which additionally contains a polar hydroxyl group.
- 4 An acrylic composition as claimed in claim 3, wherein the linking compound is selected from hydroxyethylmethacrylate, hexanedioldiacrylate or tripropylglycolmethacrylate.
- 5 An acrylic composition as claimed in any one of claims 1 - 4, wherein the finely divided oxide compound comprises colloidal silica.
- 6 An acrylic composition as claimed in any preceding claim, wherein the finely divided oxide compound has an average particle size between 1 and 50 nm.
- 7 An acrylic composition as claimed in any preceding claim, wherein the ratio of said linking compound to said finely divided oxide is preferably in the range 1:1 - 5:1 by weight.
- 8 A polymerisable composition comprising at least 70% w/w of at least one polymerisable acrylic monomer, 0.2 - 5% w/w of a finely divided compound comprising at least one oxide selected from silicon, titanium, zirconium and aluminium oxides, and 0.2 - 25% w/w of at least one linking compound which is miscible with said polymerisable acrylic compound and which is capable of bonding to the surface of the oxide compound.
- 9 a process for forming an acrylic composition comprising the steps of:
  - (a) mixing together

- (i) 70 - 99.5 % w/w of a polymerisable acrylic monomer or a solution of a polymer in a polymerisable acrylic monomer with
  - (ii) 0.5 - 30% w/w of a dispersion comprising 20 - 50% w/w of a finely divided compound selected from the oxides of silicon, titanium, zirconium or aluminium
  - (b) adding to said mixture a quantity of one or more initiator(s) which is sufficient to initiate polymerisation of the acrylic monomer under the conditions used; and
  - (c) causing the acrylic monomer to polymerise.
- 10 An acrylic composition as claimed in any of claims 1 - 8 which is in the form of a sheet, powder, pellet or bead.